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# RESERVE COPY, PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Manufacture and Use of Pigment Preparations

We, C I B A LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Various methods of bringing pigments into a fine state of dispersion are known. Thus, among other methods, it has been proposed to subject a pigment together with a kneadable substance to intensive working, for example, on a roller apparatus or kneading apparatus of the Werner-Pfleiderer system, for a prolonged period. Pigments have also been disintegrated in colloid mills of various constructions, especially in the so-called oscillation mills. By certain of these methods it is possible to produce with greater or less facility aqueous dispersions of a very wide variety of pigments, such as insoluble azo dyestuffs, vat dyestuffs, copper phthalocyanine as well as other phthalocyanines, in a good degree of dispersion, and it also well known to use such aqueous dispersions of pigments or the dry preparations obtained by suitably drying the dispersions for spinning coloured artificial silk of regenerated cellulose.

It has also been proposed to subject pigments to a powerful mechanical treatment in a roller apparatus or in a kneading apparatus together with plastic masses based on cellulose esters or ethers in order to produce products which are suitable for spinning coloured cellulose acetate artificial silk or for incorporation in lacquers or similar plastic masses.

However, such processes have not been successful in practice in all cases. Accordingly, there is still need for a process which will enable comparatively easily accessible aqueous dispersions of pigments such as can be produced by the methods referred to above, to be converted into such a form that they can be used without loss or without any substantial loss in the degree of dispersion for other purposes in which solubility in organic solvents or compatibility with the corresponding plastic substances is required.

The present invention provides a process for the manufacture of pigment preparations, wherein an aqueous suspension comprising a pigment in a state of fine division and a dissolved water-soluble salt of a carboxylated vinyl ester polymer (as hereinafter defined) is treated with an acid and/or with a salt capable of forming with the polymer a water-insoluble salt, so as to form a precipitate comprising a mixture of the pigment with the said polymer in the form of the free acid and/or a water-insoluble salt of such polymer.

The term "carboxylated vinyl ester polymer" is used herein in the interests of brevity to mean a vinyl ester polymer containing carboxyl groups which is soluble in alkalis but insoluble in water in the form of the free acid, and which is capable of being kneaded while hot and is solid at room temperature.

The aqueous suspensions of pigments in a state of fine dispersion used as starting materials in the present process can be prepared by the known methods referred to above, for example, by subjecting to

[Price]

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an intensive mechanical treatment the starting pigment, for example, a vat dyestuff, an insoluble azo dyestuff; an insoluble coloured complex metal compound, for example, a metal phthalocyanine, or another pigment, together with a kneadable substance which advantageously also possesses dispersing properties, such as sulphite cellulose waste liquor or a sodium salt of a condensation product of formaldehyde with a naphthalene sulphonation mixture containing predominantly naphthalene-2-sulphonic acid, such as is usually referred to as sodium dinaphthylmethane disulphonate. Similar products can also be obtained by subjecting to intense grinding an aqueous suspension of such a pigment, advantageously containing a dispersing agent, in a suitable colloid mill or oscillation mill. As is known it is of advantage for most purposes that the dispersion of the pigment should be very fine, for example, carried to a degree such that only a quite small fraction of the pigment particles have a size greater than  $2\mu$ , while advantageously the greater part of the particles are between about  $0.4\mu$  (the normal limit of resolution of the microscope) and  $1\mu$ , or are even finer. Such pigment suspensions are essentially useful for the present invention irrespective of the particular way in which they have been prepared.

The carboxylated vinyl ester polymers which are required for the present process, owing to the presence of carboxyl groups in the molecule, possess the property of forming water-soluble salts, for example, alkali metal salts, ammonium salts or salts of other nitrogenous bases such as methylamine, ethylamine, or morpholine. However as defined above, these polymers must be insoluble in water in the form of the free acids, so that they can be precipitated from aqueous solutions of the above mentioned salts by means of acids, such as hydrochloric acid, formic acid or sulphuric acid. Soluble salts of such carboxylated vinyl ester polymers can generally also be precipitated as the corresponding water-insoluble salts by most salts of di- or polyvalent metals such as calcium chloride.

Carboxylated vinyl ester polymers as used in the present process are known. They are always based on or consist in the main of a vinyl ester copolymer or after-treated polyvinyl ester of an organic mono-carboxylic acid. Owing to the good properties and ready accessibility of vinyl or polyvinyl acetate there is generally no need to use other esters. However, if desired, other fatty acid esters such as the propionates or butyrates may be used.

The carboxylated vinyl ester polymers may be prepared by fundamentally different methods. Thus, in the first place they may be obtained by the co-polymerisation of vinyl esters (for example, vinyl acetate) and suitable unsaturated acids such as maleic acid, fumaric acid, cinnamic acid, acrylic acid, methacrylic acid or especially crotonic acid. Secondly, there come into consideration polymerisation products in which the carboxyl groups have been made free by subsequent chemical reaction, for example, by hydrolysing esters, nitriles or acid anhydrides.

Thirdly, such vinyl ester polymers can also be prepared by introducing compounds containing free carboxyl groups by chemical reactions, for example, by partially saponifying a polyvinyl ester and treating the resulting hydroxyl groups with esterifying agents which contain free carboxyl groups in the acid residue or re-esterifying polyvinyl esters with such esterifying agents. Advantageously there are used as esterifying agents dicarboxylic acids or reactive derivatives thereof such as the anhydrides of dicarboxylic acids.

In many cases it is especially advantageous to use such carboxylated vinyl ester polymers, as, owing to the presence of a relatively small number of carboxyl groups, possess only just sufficient solubility for use in the present process. There may be used, for example, as the carboxylated vinyl ester polymer a polyvinyl ester in which a part only of all the acid residues esterifying the hydroxyl groups carries a free carboxylic acid group. In the case of co-polymers from vinyl acetate and crotonic acid, it is of advantage for example, to use at least about 2 per cent. and not substantially more than 10 per cent. of crotonic acid, whereas for the re-esterification of vinyl acetate with an anhydride of a dicarboxylic acid such as maleic anhydride, succinic anhydride and especially phthalic anhydride, the proportion of dicarboxylic acid may amount to about 5—30 per cent. In all the above cases the carboxylated vinyl ester polymers may be obtained, if desired, by conducting the polymerisation together with various vinyl esters or other polymerisable substances, so that co-polymers of such compounds are obtained. Thus, for example, vinyl acetate may be polymerised together with vinyl benzoate and crotonic acid or maleic acid mono-ethyl ester, or vinyl acetate may be polymerised together with crotonic acid and a considerable quantity about 20—50 per cent., of other polymerisable substances such as vinyl chloride or ethyl acrylate. Co-polymers

of the aforesaid kind, which contain no carboxyl groups, may be converted by the third method mentioned above into carboxylated vinyl ester polymers suitable for the present process.

In certain cases it may be possible to start from a pigment suspension in which the salt of such a polyvinyl ester derivative containing carboxyl groups plays the part of a dispersing agent and in which no other dispersing agent is present. Generally, however, it is of advantage from the present process to start from pigment suspensions which contain dispersing agents which are known to be suitable as assistants for preparing fine aqueous dispersions of pigments, for example, by a wet-milling process or by mechanical working on a roller apparatus or in a kneading apparatus of the Werner Pfleiderer type, and which possess relatively low viscosity such as sulphite cellulose waste liquor or sodium dinaphthyl-methane disulphonate (see above), and to mix such preparations with a solution of a salt of one of the highly polymeric substances already mentioned. The precipitation of such pigment suspensions which is carried out in the present process may be brought about by the addition of metal salts capable of forming a water-insoluble salt with the carboxyl groups of the polymer, but advantageously by the addition of acids, that is to say by lowering the pH value.

During the precipitation the precipitated carboxylated vinyl ester polymer carries the pigment down with it from the suspension and products may be obtained which can be used directly. By precipitating with metal salts products can be obtained having higher softening points, which may be of advantage in the further working up of the products, especially in the filtration.

In many cases however, it is also of advantage to free the precipitates in a suitable manner from any water-soluble substances also carried down, which may cause trouble later on, for example, by impairing the solubility of the product in organic solvents. This can be accomplished in some cases by washing the precipitate, especially when the precipitate is thrown down in a relatively finely powdered form. It is, however, of advantage to choose carboxylated vinyl ester polymers which are still plastic at temperatures below 100° C. In such cases it is possible by repeatedly kneading the resulting precipitate at high temperature with the addition of water to remove practically the whole content of water-soluble substances in a relatively short time. Such a kneading treatment may

also exert a favourable influence on the final degree of subdivision of the pigment. The water-soluble substances to be removed are, for example, the electrolytes resulting during the precipitation and also the salts and dispersing agents derived from the original aqueous pigment suspension.

The relative proportions of the pigment and polymer are not critical and may vary within relatively wide limits depending upon the use for which the products are intended. However, it is of advantage for maintaining the degree of dispersion not to use too small a quantity of the polymer. It is desirable that the ratio of the pigment to the carboxylated vinyl ester polymer should not be substantially greater than 1:1, and advantageously about 1:2 or smaller.

The pigment preparations may, if desired, be converted into a suitable form by compression or disintegration. They consist essentially of a pigment in a fine state of dispersion and a carboxylated vinyl ester polymer as defined above, and may be used as desired and according to the properties of the polymer for a very wide variety of purposes, for example, for dyeing artificial masses.

According to compatibility tests carried out with many carboxylated vinyl ester polymers they are mostly compatible with a spinning solution to be used for spinning cellulose acetate artificial silk and with cellulose acetate itself, and if the test is positive it is possible by dissolving such a pigment preparation in an ordinary cellulose acetate silk spinning solution to produce coloured cellulose acetate artificial silk directly in the spinning process. As cellulose acetate artificial silk in this connection there comes into consideration not only fibres prepared from pure cellulose acetate, but also those which contain other cellulose esters or mixed esters or cellulose ethers.

When the polymers contained in the pigment preparations are compatible with melts of superpolyamides, such as are used for producing fibres known as "Nylon", and easily disperse therein, they can be used for producing coloured fibres from such materials directly in the spinning process. Depending on their compatibility with particular substrata these pigment preparations can also be used for colouring masses to be used for injection moulding or for colouring a very wide variety of lacquers. If the pigment preparations used as starting material exhibit a sufficiently fine state of dispersion artificial masses are obtained which are to a great extent transparent notwithstanding that a pig-

ment is being used for colouring.

The following examples illustrate the invention, the parts and percentages being by weight:—

EXAMPLE 1.

There is introduced into a kneading apparatus capable of being heated and working on the Werner-Pfleiderer system a press cake having a known content of the pigment dyestuff from diazotised 2-methyl-4-chloro-1-aminobenzene and 1-(2'-oxy-3'-naphthoyl)-amino-2-methyl-4-chlorobenzene and such a quantity of sodium dinaphthyl methane disulphonate as dispersing agent that the ratio of dyestuff to dispersing agent is 1:1.7. The still relatively thinly fluid mass is subjected to evaporation by heat until it has the consistency of a rather thick paste. The latter is treated on a 3-roller mechanism until the degree of dispersion desired for colouring masses is obtained. By determining the content of dry solids in the paste its pigment content can be calculated, because the ratio of pigment to dispersing agent is known.

A paste so prepared is then diluted with water, for example, in a kneading apparatus, until its content of dyestuff is 8 per cent.

40 grams of a solution of 50 per cent. strength in methyl alcohol of the polymerisation product from 95 per cent. of vinyl acetate and 5 per cent.

of crotonic acid are treated with a mixture of 3 cc. of concentrated ammonia solution (density=0.91) and 160 cc. of water until dissolution is complete. The solution is introduced into 125

grams of the above described dyestuff dispersion of 8 per cent. strength, and the whole is carefully stirred. The mixture is then acidified by stirring in 10 cc. of concentrated hydrochloric acid, whereupon

the polymerisation product precipitates and carries the pigment down with it. A coarse-grained to lumpy precipitate, which occludes all the pigment, is obtained. The precipitate is separated by

filtering with suction, washed for a short time with cold water, and the mass is introduced into a kneading apparatus capable of being heated. In order to remove water-soluble constituents still

present it is kneaded with about twice its weight of water 3 times for 15 minutes on each occasion at 60—80° C. Finally the kneaded product, which still contains some water, is dried at 80° C. in a

vacuum chamber. The rather brittle mass obtained upon cooling can be disintegrated well and dissolves easily when stirred into a solution of 15 per cent.

strength of acetyl-cellulose in acetone to yield the degree of fineness originally

attained in the roller apparatus.

Instead of ammonia, another water-soluble base, such as a nitrogenous base (for example, morpholine) or a caustic alkali may be used for dissolving the polymerisation product.

A product having similar properties is obtained by using, instead of the pigment mentioned above, the dyestuff obtained from diazotised 2:5-dichloro-1-aminobenzene and 1-(2'-oxy-3'-naphthoyl)-amino-2:5-dimethoxybenzene, and in other respects proceeding in the same manner.

The polymerisation product from vinyl acetate and crotonic acid may be prepared as follows:—

95 parts of vinyl acetate, 5 parts of crotonic acid and 1 part of benzoyl peroxide are dissolved in 15 parts of methanol, and caused to polymerise by boiling. After 20 hours a further 0.13 part of benzoyl peroxide is added, after a total period of 28 hours the whole is diluted with methanol to give a solution containing 50 per cent. of dry solids.

EXAMPLE 2.

A mixture of 20 parts of copper phthalocyanine, 20 parts of sodium dinaphthylmethane disulphonate and 20 parts of water is brought on a 3-roller mechanism in the manner described in Example 1 to the degree of dispersion desired for colouring masses. By diluting the resulting paste with water a pigment dispersion of 8 per cent. strength is likewise obtained.

A solution is prepared in a manner similar to that described in Example 1 from 40 grams of a solution of 50 per cent. strength in methyl alcohol of the polymerisation product from 98 per cent. of vinyl acetate and 2 per cent. of crotonic acid, 3 cc. of concentrated ammonia solution (density=0.91) and 160 cc. of water. The solution is added to 125 grams of the copper phthalocyanine dispersion of 8 per cent. strength, and then the polymerisation product is precipitated by acidification with 10 cc of concentrated hydrochloric acid. In precisely the manner described in Example 1, the precipitate is separated by filtering with suction, washed, treated in a kneading apparatus and dried. In this case also a product is obtained which disintegrates well and when introduced into a solution of 15 per cent. strength of acetyl cellulose in acetone dissolves readily to yield the degree of fineness attained before the precipitation.

The polymerisation product used can be prepared in precisely the manner described in Example 1, but using 98 parts

of vinyl acetate and 2 parts of crotonic acid.

#### EXAMPLE 3.

There are introduced into a kneading apparatus capable of being heated and working on the Werner-Pfleiderer system 92 parts of a press cake of the dyestuff Cibacron Blue 14S (Colour Index, 1922, No. 1106) having a pigment content of 24 per cent., and 29 parts of solid sulphite cellulose waste liquor. The whole is evaporated until a thick kneadable mass is obtained. It is then further kneaded until there is obtained the degree of dispersion desired for colouring masses.

The mixture is then diluted with water to a dyestuff content of 8 per cent. The quantity stated in Example 1 of the ammoniacal solution of the polymerisation product from 95 per cent. of vinyl acetate and 5 per cent. of crotonic acid is carefully stirred into 83 grams of the above dispersion. The polymerisation product and pigment are then precipitated as described in Example 1 by the addition of 10 cc of concentrated hydrochloric acid, the precipitate is separated by filtering with suction, treated in a kneading apparatus, and dried in a vacuum chamber. In this manner there is also obtained a product which dissolves easily in a solution of 15 per cent. strength of acetyl cellulose in acetone to yield the degree of fineness originally attained in the kneading operation.

Instead of a solution of the polymerisation product in methyl alcohol, there may be used an emulsion of the polymerisation product, which is prepared by emulsion polymerisation in an aqueous medium. The procedure is then as follows:—

A clear, thin fluid solution is prepared from 49 grams of the above emulsion (containing 49 per cent. of dry solids) by stirring it with a mixture of 200 grams of water and 4.5 cc of concentrated ammonia solution (density=0.91). The solution is added to 100 grams of the above described dyestuff dispersion of 8 per cent. strength, and then the polymerisation product and pigment are precipitated by acidification with 10 cc of concentrated hydrochloric acid. The precipitate is separated by filtering with suction, treated in a kneading apparatus at 80–90° C., and dried in a vacuum chamber, whereby a quite similar pigment preparation is obtained.

#### EXAMPLE 4.

A mixture of 10 parts of the dyestuff from diazotised ortho-nitro-para-toluidine and acetoacetic acid anilide, 15 parts of

sodium dinaphthyl-methane disulphonate and 75 parts of water is introduced into a "Vibratom" oscillation mill, and the mixture is ground until it has attained the degree of dispersion desired for colouring masses. The paste so obtained is diluted with water to a dyestuff content of 7 per cent.

A copolymer of vinyl acetate and maleic acid mono-methyl ester is prepared as follows:—

1 part of vinyl acetate, 0.15 part of maleic anhydride and 0.02 part of benzoyl peroxide are dissolved in 0.3 part of methanol. 0.5 part of the resulting mixture (amounting to 1.47 part) is first pre-polymerised for 3 hours at the boil. Then there is continually added to the reaction mass, firstly, the remainder of the mixture in the course of 3 hours, and, secondly, in the course of 2 hours a solution of 0.075 part of maleic anhydride in 0.15 part of methanol, the polymerisation is completed in a further 3 hours, and then the whole is diluted with methanol to give a solution of 56 per cent. strength.

As maleic anhydride is very rapidly converted into the mono-methyl ester in the presence of methanol, this mono-ester serves as the polymerisable unsaturated acid for the copolymerisation.

42.8 parts of the solution of 56 per cent. strength of the polymerisation product are then treated with a mixture of 200 grams of water and 9 cc of concentrated ammonia solution (density=0.91) until dissolution takes place.

The resulting solution is introduced into 114 grams of the above dyestuff dispersion of 7 per cent. strength, and the whole is well mixed. The pigment and polymerisation product are then precipitated by stirring in 16 cc of concentrated hydrochloric acid, and the precipitate is separated by filtering with suction, treated with fresh water 3 times for 15 minutes on each occasion in a kneading apparatus capable of being heated, and dried in a vacuum chamber. The resulting product can be disintegrated well in the cold.

#### EXAMPLE 5.

A copolymer of vinyl acetate, vinyl chloride and crotonic acid is prepared in the following manner:—

26 parts of vinyl acetate, 2 parts of crotonic acid and 0.6 part of benzoyl peroxide are dissolved in 20 parts of acetone, charged into an autoclave fitted with stirring mechanism, and therein mixed with 12 parts of vinyl chloride. The autoclave is then maintained at about 80° for 21 hours, cooled, and discharged. A weakly turbid solution is obtained having a content of dry solids of 52 per cent. The

dry residue has a chlorine content of 19.7 per cent., which corresponds to a vinyl chloride content of 35 per cent.

- 38.7 grams of the solution of 52 per cent. strength of the polymerisation product are stirred with a mixture of 200 grams of water and 8 cc of concentrated ammonia solution until dissolution is complete. The resulting solution is introduced into 143 grams of the dyestuff dispersion of 7 per cent. strength described in Example 4. The polymerisation product and pigment are then precipitated by means of 12 cc of concentrated hydrochloric acid, the precipitate is separated by filtering with suction, treated at 80° C. in a kneading apparatus and dried in a vacuum chamber. The cooled product can be disintegrated well.

#### 20 EXAMPLE 6.

A copolymer of vinyl acetate, vinyl benzoate and crotonic acid is prepared as follows:—

- 45 parts of vinyl acetate, 12 parts of vinyl benzoate, 3 parts of crotonic acid and 0.6 part of benzoyl peroxide are dissolved in a mixture of 7.2 parts of isopropanol and 1.8 parts of water, and polymerised at the boil. After 7 hours a further addition of 0.18 part of benzoyl peroxide is introduced, and after a further 11 hours a highly viscous solution is obtained, which is diluted with methanol to a content of dry solids of 36 per cent.

- 35 From 56.2 grams of the polymer solution of 36 per cent. strength a clear thinly fluid solution is prepared with a mixture of 150 cc of water and 5 cc of concentrated ammonia solution. The resulting solution is mixed with 143 grams of the dyestuff dispersion of 7 per cent. strength mentioned in Example 4, the polymer and pigment are precipitated by means of 8 cc of concentrated hydrochloric acid, and the precipitate is separated by filtering with suction, treated in a kneading apparatus at 60–70° C., and dried in a vacuum chamber.

- The products obtained as described in 50 Examples 4, 5 and 6 dissolve easily when introduced into a solution of 15 per cent. strength of acetyl cellulose in acetone to yield the state of fineness attained in the oscillation mill.

#### 55 EXAMPLE 7.

A copolymer of vinyl acetate, ethyl acrylate and crotonic acid is prepared as follows:—

- 42 parts of vinyl acetate, 15 parts of 60 ethyl acrylate and 3 parts of crotonic acid are polymerised under the same conditions as those used in Example 6, and then diluted with methanol to a solution of 50 per cent. strength.

40 grams of the polymer solution of 65 50 per cent. strength are treated with a mixture of 180 cc of water and 4 cc of concentrated ammonia solution, whereby a thinly fluid turbid solution is obtained. The latter is mixed with 125 grams of 70 the dyestuff dispersion of 8 per cent. strength described in Example 1, and the polymerisation product and pigment are precipitated by means of 8 cc of concentrated hydrochloric acid and the residue 75 is separated by filtering with suction, treated at 60–70° C. in a kneading apparatus and dried in a vacuum chamber. The resulting product can be disintegrated well, and dissolves when introduced in acetyl cellulose solution to yield 80 the state of fineness attained in the roller mechanism.

#### EXAMPLE 8.

A mixture of 10 parts of Indigo, 10 85 parts of sodium dinaphthyl methane disulphonate and 80 parts of water is introduced into a "Vibratom" oscillation mill. Grinding is continued until the degree of dispersion desired for colour- 90 ing masses is obtained. The resulting paste is diluted with water to a dyestuff content of 8 per cent.

A polymerisation product containing free carboxyl groups is prepared in the 95 following manner:—

Vinyl acetate is polymerised in the presence of isopropanol using benzoyl peroxide as catalyst to yield a polyvinyl acetate of low viscosity. (A solution of 0.3 100 gram of solid substance in 100 cc of acetone has a relative viscosity of 1.04 at 20° C.).

The resin solution is hydrolysed or re-esterified to an ester number of about 105 600 by the addition of methanol and hydrochloric acid, and then the product is neutralised and evaporated to dryness.

1 part of the resulting polyvinyl acetate derivative containing hydroxyl groups is 110 melted with 0.08 part of phthalic anhydride for one hour at 150–170° C., and then cooled, whereby a solid mass is formed.

180 grams of the latter product are 115 then finely pulverised, stirred with 1600 grams of water and, after the addition of 30 grams of concentrated ammonia solution (density=0.91) treated until dissolution is complete. The resulting solution 120 is mixed with 1125 grams of the above Indigo dispersion of 8 per cent. strength. The artificial material and pigment are then precipitated by the addition of 40 grams of concentrated formic acid (85 125 per cent. strength). The whole is heated to 35° C., filtered, and the filter residue is washed until neutral with water. The resulting filter residue is placed in a 2-

roller mechanism heated at 120—130° C.; and treated until all the water has evaporated. The cooled product can be disintegrated well, and dissolves easily when introduced into an acetyl cellulose solution to yield the degree of fineness attained in the oscillation mill.

Instead of drying the filter residue on a 2-roller mechanism, it may be dried in a vacuum chamber. In this case, in order to eliminate any harmful pigment agglomerations still present, it is treated on a heated 2-roller mechanism.

#### EXAMPLE 9.

Instead of bringing about precipitation of the artificial material by lowering the pH value, it can be brought about by reaction with salts of polyvalent metals, for example, in the following manner:—

20 grams of the polymerisation product mentioned in Example 8 are completely dissolved by treatment with 180 cc of water and 3.7 cc of concentrated ammonia solution. The resulting solution is introduced into 125 grams of the Indigo dispersion of 8 per cent. strength mentioned in Example 8. By the addition of an aqueous solution of 3 grams of calcium chloride the calcium salt is precipitated as well as the pigment. The whole is heated to 30° C., filtered with suction, and the filter residue is treated at 60° C. in a kneading apparatus and dried in a vacuum chamber.

The resulting product can be disintegrated well and dissolves in an acetyl cellulose solution to yield the degree of fineness attained in the oscillation mill. From the product precipitated with calcium chloride the metal-free preparation can be recovered by thoroughly kneading the precipitate obtained as described above with dilute acetic acid, instead of with water, and then further proceeding in the manner described above.

#### EXAMPLE 10.

A polymerisation product containing free carboxyl groups is prepared in the following manner:—

The polyvinyl acetate of low viscosity obtained as described in the second paragraph of Example 8 is hydrolysed in the manner described above until its ester number is about 500, and melted with 0.25 part of phthalic anhydride per one part of the hydrolysed product.

20 grams of the resulting polymerisation product are then pulverised, and treated with a mixture of 180 cc of water and 8 cc of concentrated ammonia until dissolution is complete. The resulting solution is introduced into 125 grams of the Indigo dispersion described in

Example 8. The polymer and pigment are precipitated by stirring in 16 cc of concentrated hydrochloric acid, separated by filtering with suction, treated at 60° C. in a kneading apparatus, and dried in a vacuum chamber. The resulting product dissolves easily in a solution of acetyl cellulose in acetone to yield the state of fineness obtained in the oscillation mill.

#### EXAMPLE 11.

A polymerisation product containing free carboxyl groups is prepared in the following manner:—

1 part of the hydrolysed product obtained as described in the second paragraph of Example 8 and having an ester number of 600 is melted with 0.073 part of maleic anhydride. In this case the maleic anhydride does not react as a polymerisable compound by reason of its double bond, but as a dicarboxylic anhydride with the formation of a semi-ester containing free carboxyl groups.

20 grams of the latter product are pulverised, and completely dissolved by means of a mixture of 180 cc of water and 6 cc of concentrated ammonia solution. The solution is added to 125 grams of the dyestuff dispersion of 8 per cent. strength described in Example 8, and then the polymerisation product and pigment are precipitated by acidification with 12 cc of concentrated hydrochloric acid. The precipitate is separated by filtering with suction, treated in a kneading apparatus and dried in a vacuum chamber. The product so obtained dissolves easily in a solution of acetyl cellulose in acetone to yield the degree of fineness attained in the oscillation mill.

#### EXAMPLE 12.

0.5 gram of the pigment preparation obtained as described in Example 1 and containing 33.3 per cent. of dyestuff, is added to a cellulose acetate artificial silk spinning mass consisting of 600 cc of acetone, 100 grams of acetyl cellulose, 3 grams of lactic acid ethyl ester and 4 grams of paraffin oil. The whole is stirred well, allowed to stand for one hour and further stirred for a short time which suffices to disperse the dyestuff completely. Threads obtained from the resulting mass by dry spinning in the usual manner exhibit a brilliant bluish red colour possessing very good properties of wet fastness.

If in this Example the aforesaid pigment preparation is replaced by 0.75 gram of the preparation obtained as described in Example 8, the filaments obtained have a reddish-blue colour which also possesses very good properties of wet fastness.



## EXAMPLE 13.

A paste consisting of 675 parts of acetyl cellulose, 325 parts of dimethyl glycol phthalate and 1000 parts of acetone is placed on a 2-roller mechanism capable of being heated. 0.3 part of the pigment preparation obtained as described in Example 1 is added, and the whole is rolled at 130° C. whereby the dyestuff is very rapidly dispersed and the rolled material is coloured uniformly and completely. After evaporating the acetone the mass is rolled into the form of a sheet, the latter is disintegrated, and plates 2 mm. thick are produced therefrom in an injection moulding machine. These plates have a completely uniform red and transparent colour.

## EXAMPLE 14.

A mixture of 13 parts of polyvinyl chloride, 7 parts of dioctyl phthalate and 0.16 part of the dyestuff preparation obtained as described in Example 3 is applied to a 2-roller mechanism heated at 130° C. Upon rolling, the dyestuff is very rapidly disintegrated and transparent foil having a strong blue colour is obtained.

## EXAMPLE 15.

The pigment preparations obtained as described in Examples 1—11 can be used for dyeing lacquers, for example, in the following manner:—

10 grams of the pigment preparation obtained as described in Example 2 are triturated in a mortar with a small quantity of spirit varnish (damar resin in alcohol). Then the total quantity of lacquer, for example, about 1 litre, is added in portions with further trituration. When the lacquer is coated on aluminium foils a strong transparent coloured coating is obtained.

What we claim is:—

1. A process for the manufacture of pigment preparations, wherein an aqueous suspension comprising a pigment in a state of fine division and a dissolved water-soluble salt of a carboxylated vinyl ester polymer (as hereinbefore defined) is treated with an acid and/or with a salt capable of forming with the polymer a water-insoluble salt, so as to form a precipitate comprising a mixture of the pigment with the said polymer in the form of the free acid and/or a water-insoluble salt of such polymer.

2. A process as claimed in Claim 1, wherein the precipitate so obtained is subjected to a mechanical treatment or thorough kneading at a raised temperature.

3. A process as claimed in claim 2, wherein the mechanical treatment or thorough kneading is carried out before

or during drying.

4. A process as claimed in Claim 1, 2 or 3, wherein a copolymer of a vinyl ester and unsaturated acid is used as the carboxylated vinyl ester polymer.

5. A process as claimed in Claim 4, wherein a copolymer prepared from 90—98 per cent. of vinyl acetate and 10—2 per cent. of crotonic acid is used.

6. A process as claimed in Claim 1, 2 or 3, wherein a copolymer of a vinyl ester and an unsaturated acid together with another compound capable of copolymerising with vinyl esters is used as the carboxylated vinyl ester polymer.

7. A process as claimed in Claim 1, 2 or 3, wherein there is used as the carboxylated vinyl ester polymer a polyvinyl ester in which a part only of all the acid residues esterifying the hydroxyl groups carries a free carboxylic acid group.

8. A process as claimed in Claim 7, wherein a partially hydrolysed polyvinyl acetate subsequently esterified with a dicarboxylic anhydride, in which the proportion of polyvinyl acetate amounts to 70—95 per cent. and the proportion of the dicarboxylic acid to 30—5 per cent., is used.

9. A process as claimed in any one of claims 1—8, wherein there is used a carboxylated vinyl ester polymer which is compatible with a cellulose acetate artificial silk spinning solution and with cellulose acetate.

10. A process as claimed in any one of claims 1—9, wherein the ratio of the pigment to the carboxylated vinyl ester polymer is not substantially greater than 1:1, and is advantageously about 1:2 or smaller.

11. A process for the manufacture of a pigment preparation conducted substantially as described in any one of Examples 1—11 herein.

12. A pigment preparation which has been obtained by the process claimed in any one of claims 1—11.

13. A process for colour spinning cellulose acetate artificial silk, in which a pigment preparation claimed in claim 12 is used.

14. A process for colouring lacquers, in which a pigment preparation claimed in claim 12 is used.

15. A process for colouring injection moulding masses, in which a pigment preparation claimed in claim 12 is used.

16. A process for colouring artificial masses, in which a pigment preparation claimed in claim 12 is used.

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